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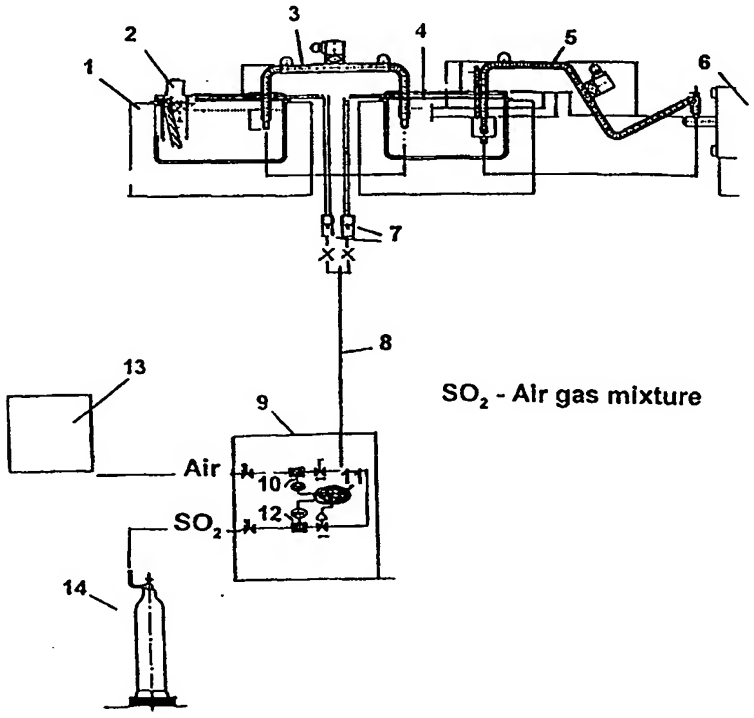
(54) Title: METHOD OF FLUXLESS MELTING OF MAGNESIUM

(57) Abstract

Fluxless melting of magnesium (alloy) metal applying a gas mixture of dry air and SO_2 as protection atmosphere is provided where a constant pre–set level of SO_2 is maintained by means of two mass flowmeters where one of them is in control of the other.



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Method of fluxless melting of magnesium

The present invention concerns a method of fluxless melting of magnesium, and more particularly a method of mixing and controlled feeding of protection gas to melting/holding furnaces and apparatus applied by such method.

Magnesium (metal) is known for its high affinity to oxygen and high vapour pressure of molten Mg (alloys) causing operational problems.

Currently SF6 based gas is used by most magnesium die casters for protection against oxidation of molten magnesium metal. Until recently the use of SF6 was not considered to represent any environmental hazard being non-toxic and without negative impact on the working atmosphere in the foundries. However, due to its very high calculated greenhouse warming potential strict restrictions on the use of the gas in applications causing emission to the atmosphere are expected in the near future.

Consequently, a search for an alternative protection medium has focused on switch back to SO_2 originally applied by the industry prior to the introduction of SF6 gas.

It is well known that SO_2 atmosphere strongly reduces the oxidation of molten magnesium by modifying the surface film and that producers of primary metal, sand and die casters have been using SO_2 in gas form or generated (in situ) by adding sulphur powder to furnaces.

SO_2 is, however, toxic. In high concentrations and in contact with humidity it results in enhanced corrosion of steel equipment. The present occupational exposure limit in Norway is 2 ppm over an 8 hours period of time corresponding to a concentration of 5 mg/m^3, and corresponding limits in Germany and North America are similar.

Consequently, it is an object of the present invention to provide a new and improved method of mixing and maintaining a pre-set level of SO_2 in an air mix within narrow tolerances.

Another object of the present invention is to provide an apparatus ensuring environmentally safe mixing and feeding of the SO_2 air mix into the Mg-furnaces/vessels.

Still another object of the present invention is to provide an improved method of fluxless melting of magnesium substantially reducing problems connected to formation of scaling on the crucible walls.

These and other objects and features are met by provision of the new method and apparatus according to the present invention as it appears from the attached patent claims 1-5.

The new method of mixing and maintaining of the pre-set level of SO_2 in the air mix will now be described and readily understood from the following description under reference to the accompanying drawings, Figs. 1-3, and preferred embodiments/modes of operation, where

Fig. 1 shows schematically a flow chart of the mixing/feeding process,

Fig. 2 illustrates schematically in a vertical, partial cross-section a feeding arrangement (apparatus) usable in the process of fluxless melting of magnesium, and

Fig. 3 shows schematically the applied furnace/vessel in a horizontal cross-section along line I–I

Referring to Fig. 1 illustrating schematically a flow chart of the mixing/feeding process applicable according to the present invention, a melting furnace 1 is equipped with charging device 2 to feed solid magnesium into the furnace, transferring device, e.g. transfer tube 3 to move subsequently the Mg-melt into and adjacent casting unit (furnace) here depicted as 4. By means of e.g. so-called gas displacement (metering) pump 5 the melt is fed in a controlled manner (doses) into any suitable casting equipment, e.g. the shown high pressure die casting machine 6.

According to the present invention and as an example of a preferred embodiment an apparatus arrangement for controlled mixing/feeding of the mixture SO_2/dry air comprises a compressor 13 and a pressure bottle 14 providing (dry) air and SO_2 gas, respectively, into the mixing device 9 comprising a mass flowmeters 10 and 12 for the air and SO_2, respectively, and a control steering unit 11 to ensure an adequate pre-set concentration of SO_2 in the gas mixture. The resulting gas mixture is then conducted through a feeding line 8 and distributed by means of manifolds (flowmeters) 7 and customary valves into the actual (part of) furnaces 1 and 4.

This is achieved by applying a double set of mass flowmeters 10,12 where the mass flowmeter 10 controlling the air flow is also in control of the mass flowmeter 12 so that the concentration of SO_2 in the gas mixture will never exceed the pre-set level. In the case of an emergency situation, e.g. break down on the feeding line/equipment providing dry air, this "master" flowmeter 10 will automatically switch off also feeding of SO_2.

As "dry air" referred to in the description air having a dew point - 30°C is applied.

Using this sophisticated mixing unit ensures that the SO_2 concentration may be kept very low and the distribution of the protection gas to the liquid. Mg surface is so uniform that emissions from furnace atmospheres to surroundings will be negligible and represents no hazard for foundry personnel.

With references to Figs. 2 and 3 illustrating schematically an arrangement of feeding means usable in the process of feeding/distribution of SO_2/air mixture according to the present invention, Fig. 2 shows schematically in a partial, vertical cross-section the furnace 1 as a steel vessel accommodated in a thermally insulated furnace shell 20. The melting furnace is provided with a charging device 2 to introduce solid Mg into the furnace, a baffle plate 15 dividing the furnace into a charging sector and a main body of the melting furnace where the furnace design/configuration should assure a high ratio volume/surface area in order to minimise reaction(s) occurring between molten Mg and the atmosphere. Consequently, all lids and hatches must also be well tightened as illustrated in an exploded view showing details of lid seals 16. The gas mixture is provided to the furnace(s) through a sophisticated distribution system allowing the gas mixture to be evenly distributed close to the melt surface, e.g. by means of a ring tube 17 positioned along the furnace periphery in the vicinity of the melt surface as shown in Fig. 3. Fig. 3 illustrating schematically the applied melting furnace 1 in a horizontal cross-section taken along line I–I in Fig. 2, further depicts the charging zone (device) 2, dividing baffle plate 15 and a lid 19 for eventual removal of dross/sludge from the furnace.

The ring tube 17 is provided with a plurality of apertures ensuring an even distribution of the protective gas mixture by controlled directional impingement of the melt surface.

Experiments conducted in industrial size furnaces with SO_2 air mixtures applying the above method confirm that the SO_2/air protection atmosphere protects effectively molten magnesium surfaces against oxidation.

The following reactions between the metal and the gas mixture may occur:

$$Mg(l) + O_2 + SO_2 \rightarrow MgSO_4(s)$$

$$MgSO_4(s) + Mg(l) \rightarrow MgO(s) + Mg(s)$$

$$MgS(s) + O_2 + SO_2 \rightarrow MgSO_4(s)$$

$$MgO(s) + SO_2 + O_2 \rightarrow MgSO_4(s)$$

It is believed that a sort of "self-reparation" of possibly disrupted/cracked layers of MgO(s) + MgS(s) occurs due to a further reaction between magnesium evaporated through such cracked opening and the cover gas.

Example 1

Summary of pilot trials conducted in full scale furnaces in laboratory:

Temperature of the melt	:	655-690°C
Gas mixture flow rate /m^2 melt surface	:	10l/min
SO_2 concentration in the gas mixture	:	0.5-1.7%
Duration of trials	:	47 hours

Example 2

Tests have been carried out on an industrial scale in a hot-chamber casting machine. A mixing unit built according to the present invention provided SO_2/dry air mixture for the furnace. Gas samples were frequently monitored (every four hours) both from the mixing unit, the furnace atmosphere and the working atmosphere as well.

Melt surface area	:	0.3 m^2
Melt temperature	:	660°C
Flow rate of the gas mixture	:	7.3 l/min
Duration of trials	:	3 days
SO_2 concentration in the (dry) air mixture	:	0.8%
SO_2 concentration in the atmosphere	:	0.2 ppm

Gas samples of the atmosphere were collected at three differenct locations in the foundry - at operator level, in the vicinity of the charging lid and approximately 3 m above the floor. No significant differences were measured in the gas concentrations between the locations indicating a safe, controlled operation and an adequate ventilation of the foundry hall.

A controlled diluted SO_2/air mixture was provided and maintained during the test periods, something being of crucial importance also for the life time of the applied steel equipment.

It is well known that both SO_2 and SF6 in contact with humidity will accelerate steel corrosion. Deposits and reaction products may be formed on e.g. crucible/furnace walls, something which under unfavourable conditions can lead to metal eruptions from the furnace. Consequently, high concentration of SO_2 combined with high humidity should be avoided.

Claims

1. Method of fluxless melting of magnesium and magnesium alloy metal comprising mixing of sulphur dioxide (SO_2) and dry air and maintaining a protection gas-mixture atmosphere above molten metal,
characterised in that
a constant pre-set level of SO_2 is maintained in the gas-mixture regardless of variations in actual gas-mixture consumption by means of at least two mass flowmeters (10,12) controlling the flow of dry air and SO_2, respectively, where the dry air flowmeter (10) controls the SO_2 flowmeter (12).

2. Method according to claim 1,
characterised in that
the concentration of SO_2 in the gas-mixture is in the range from 0.1 to 5 weight%.

3. Method according to claim 2,
characterised in that
the SO_2 concentration is from 0.2 to 1.5 weight%.

4. Apparatus for mixing/feeding of a protection gas-mixture comprising sources of dry air (13) and SO_2 gas (14) and mixing device (9) comprising a mass flowmeter (10) for dry air and a mass flowmeter (12) for SO_2 gas and steering unit (11) for monitoring and maintaining the composition and flow of the gas-mixture
characterised in that
the air mass flowmeter (10) is also in control of/steering the SO_2 gas flowmeter (12).

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5. Apparatus according to claim 4,
characterised in that
the mass flowmeters (10,12) are digital mass flowmeters.

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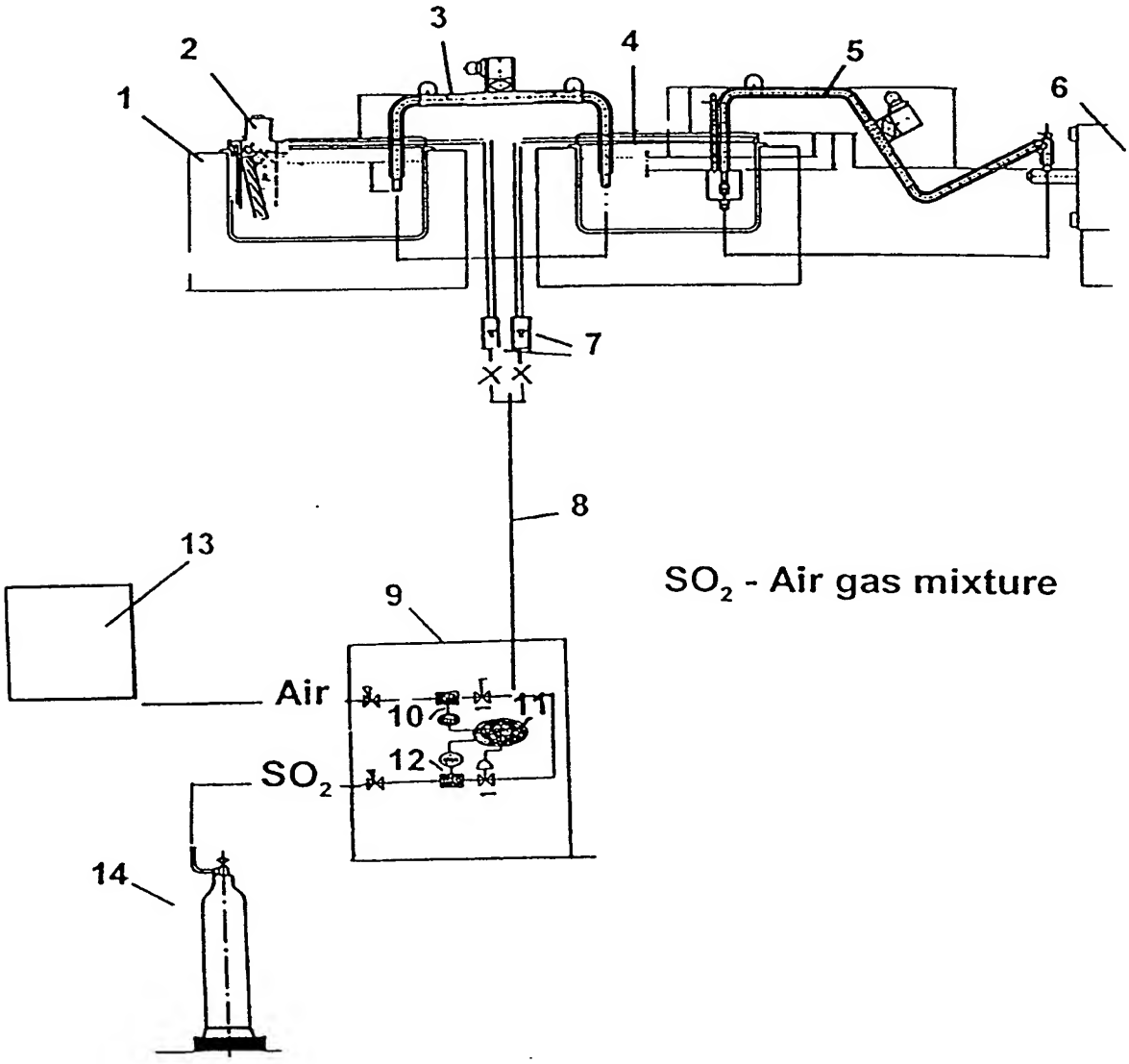

Fig. 1

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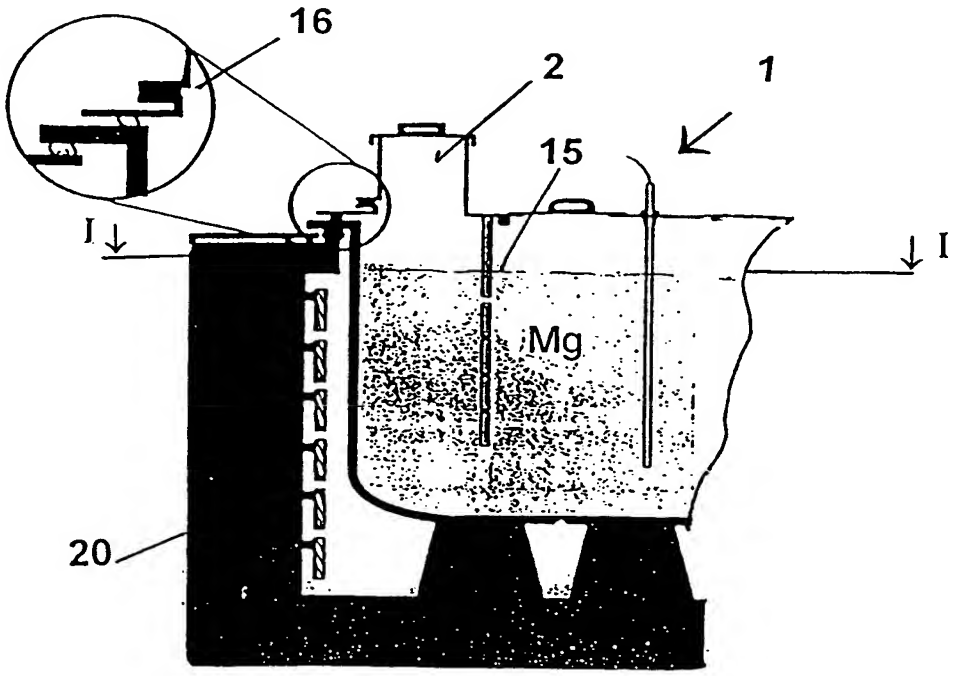

Fig. 2

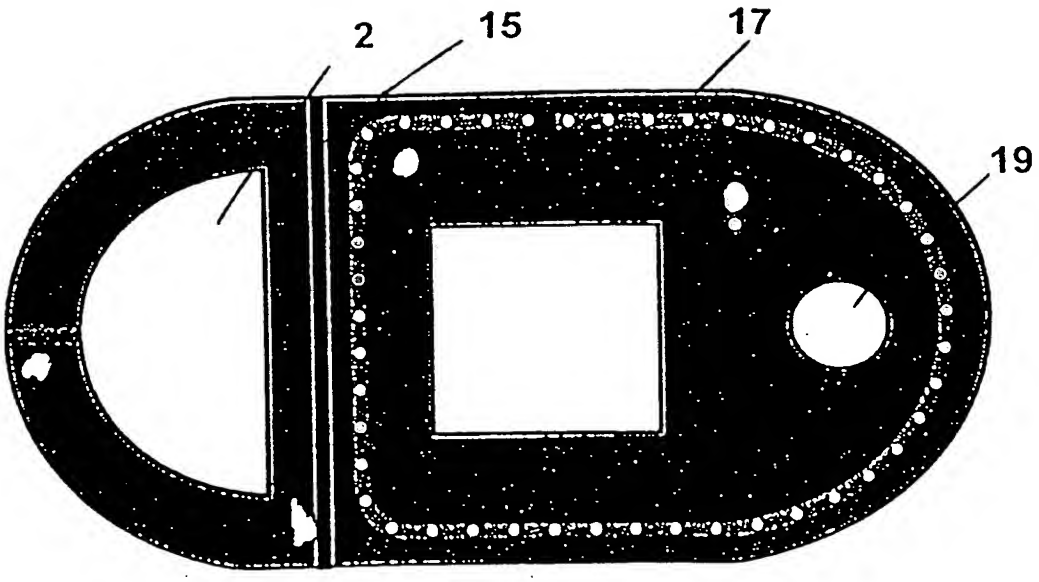

Fig. 3

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 98/00200

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B22D 21/04, F27D 7/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B22D, C22B, F27D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9721510 A1 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION), 19 June 1997 (19.06.97), page 7, line 23 - line 31; page 15, line 3 - line 16, claim 16	1-3
Y	US 4478270 A (HYMAN ROSENTHAL ET AL), 23 October 1984 (23.10.84), column 7, line 13 - line 29, abstract	1-3
A	US 4550763 A (IVAN D. NIKOLOV), 5 November 1985 (05.11.85), column 5, line 20 - column 6, line 14	1-3

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
21 October 1998	30-10-1998
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Mårten Hulthén Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 98/00200

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 2018407 A (FRUEHLING, JAMES WILLIAM ET AL), 25 February 1971 (25.02.71), claims 1,9-10 --	1-3
A	EP 0531810 A2 (LOI ESSEN INDUSTRIEOFENANLAGEN GMBH), 17 March 1993 (17.03.93), claims 1-2, abstract --	1-3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/N098/00200

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO98/00200

I. Claims 1-3 relate to a method of fluxless melting of magnesium or a magnesium alloy comprising creating a protective atmosphere above the molten metal.

II. Claims 4-5 relate to an apparatus for mixing/feeding of a protection gas mixture. The claims do not involve melting of magnesium or any other metal.

These groups of inventions are not so linked as to form a general inventive concept.

INTERNATIONAL SEARCH REPORT

Information on patent family members

27/07/98

International application No.
PCT/NO 98/00200

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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